Dihedral angles			
O(1)—N(1)—O(7′)/ O(3)—N(2)—N(3′)	21.4	22.4	25.3 (1)
O(2′)—O(5)—O(w1)/ O(3)—N(2)—N(3′)	5.3	4.9	6.5 (2)

* Ionic radii of the trivalent ions with eight coordination bonds from Lide (1991).

Table 3. *Selected distances* (Å) *and torsion angles* (°) *for* $[M_2(15\text{-dten})_2(H_2O)_2].14H_2O$, *where M* = Y *or* La

	Y	La
C(1)—O(1)	1.25 (1)	1.253 (4)
C(8)—O(2)	1.24 (1)	1.243 (4)
C(12)—O(3)	1.26 (1)	1.262 (4)
C(12)—O(4)	1.26 (1)	1.239 (4)
C(14)—O(5)	1.28 (1)	1.257 (4)
C(14)—O(6)	1.29 (1)	1.249 (4)
C(16)—O(7)	1.27 (1)	1.274 (4)
C(16)—O(8)	1.26 (1)	1.238 (4)
C(1)—N(5)	1.34 (1)	1.307 (4)
C(8)—N(4)	1.33 (1)	1.313 (4)
C(9)—N(4)—C(8)—O(2)	−7.9 (13)	−7.4 (5)
C(9)—N(4)—C(8)—C(7)	168.7 (7)	168.9 (3)
C(10)—N(5)—C(1)—O(1)	−0.6 (14)	−0.7 (5)
C(10)—N(5)—C(1)—C(2)	178.7 (8)	177.4 (3)

The H atoms bonded to the C or N atoms were placed at idealized positions with bond lengths of 0.95 Å. Most H atoms of the water molecules were located from the ΔF map, but some H atoms, *i.e.* those associated with the O(*w*5), O(*w*6), O(*w*7) and O(*w*8) atoms in the Y complex, and the O(*w*8) atom in the La complex, could not be located. The located H atoms were included in the structure-factor calculations as riding atoms with fixed isotropic temperature factors (B = 5 Å^2). For $[Y_2(15\text{-dten})_2(H_2O)_2]$, the *UCLA Crystallographic Package* (1984) was used for data collection and cell refinement; *SDP* (Frenz, 1978) was used to solve and refine the structure. For $[La_2(15\text{-dten})_2(H_2O)_2]$, *MolEN* (Fair, 1990) was used to solve and refine the structure and the diagrams were prepared using *ORTEP*II (Johnson, 1976).

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Lists of experimental details, structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, bond distances and angles involving H atoms, hydrogen-bonding geometry, least-squares-planes data and torsion angles, along with packing diagrams for both compounds, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71741 (53 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1049]

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(Bipyridyl-*N*,*N*′)diiodoplatinum(II)

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Abstract

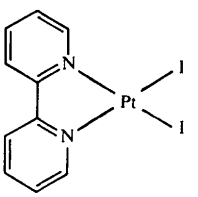
Square-planar (bipyridyl-*N*,*N*′)diiodoplatinum(II), $[PtI_2(C_{10}H_8N_2)]$, has normal Pt—N(bipyridyl) [2.029 (7) Å] and Pt—I bonds [2.589 (2) Å]. The bipyridyl ligand exhibits normal distances and angles. Because of steric effects, the intramolecular I···I separation [3.587 (1) Å] and the corresponding I—Pt—I angle [87.7 (1)°] are significantly smaller than those observed for other *cis*-bis(iodo)bis(*N*-donor) complexes. The parallel square-planar units stack to form a chain structure. Relative lateral displacement of consecutive molecules along a chain results in a Pt···Pt distance [5.291 (1) Å] considerably longer than the interplanar spacing [3.510 (11) Å].

Comment

In our work on the spectroscopy of linear-chain platinum(II) diimines, we have examined a series of Pt(bpy)X_2 complexes (X = Cl, Br, I). The bis(chloro) complex exhibits dimorphism, crystallizing in a yellow form as discrete monomer units (Textor & Oswald, 1974) and in a red form as a linear chain with a Pt···Pt separation of 3.45 Å (Textor & Oswald, 1974; Osborn & Rogers, 1974). The spectroscopic properties of the yellow bis(bromo) analogue

† Contribution No. 8826.

strongly suggest that the complex exists in a monomeric environment in the solid state. However, the interpretation of the spectroscopy of the orange bis(iodo) species is less conclusive. It is uncertain whether the orange color of the bis(iodo) complex arises from a $d\sigma^*$–π^*(bpy) charge-transfer transition associated with either a dimer or linear-chain structure, or a monomer d–π^*(bpy) charge transfer red-shifted in the relatively weak N_2I_2 ligand field. Our determination of the structure of (bipyridyl)bis(iodo)platinum(II), (1), establishes that the latter interpretation is to be preferred.



(1)

The molecule, including the numbering system, is depicted in Fig. 1 and the packing is shown in Fig. 2. The molecule lies on a twofold axis through the Pt atom. Distances and angles in the bipyridyl ligand are normal. The Pt—N bond to the bipyridyl [2.029 (7) Å] and the N—Pt—N angle [79.3 (3)°] are in close agreement with the values observed for the red form of $Pt(bpy)Cl_2$ [2.001 (6) Å, 80 (1)°] (Osborn & Rogers, 1974).

The Pt—I distance [2.589 (2) Å] is consistent with observed bond lengths in other *cis*-bis(iodo)bis(*N*-donor) complexes. However, the intramolecular I···I separation [3.587 (1) Å] and the corresponding I—Pt—I angle [87.7 (1)°] are significantly smaller than those found in *cis*-$Pt(NH_3)_2I_2$ [3.765 (1) Å, 93.40 (4)° (Raudaschl-Seiber, Lippert, Britten & Beauchamp, 1986)], *cis*-$Pt(C_3H_5NH_2)_2I_2$ [3.780 (2) Å, 94.26 (4)° (Oksanen, Kivekas, Lumme, Valkonen & Laitalainen, 1989)] and Pt(1,2-benzoquinone dioxime)I_2 [3.71 Å, 91.5 (1)° (Mégnamisi-Bélombé & Endres, 1985)]. This is a probable consequence of steric interactions involving the coplanar bipyridyl ligand and I atoms. Both the I···I intramolecular distance [3.587 (1) Å] and the I···H1 intramolecular distance [2.825 (1) Å], based on the calculated H-atom positions, are significantly shorter than the van der Waals distances.

The parallel monomer units stack to form a chain structure with consecutive molecules rotated by 180° (Fig. 2). Viewed on projection down the *b* axis, the chain of molecules is parallel to the *c* axis and makes a non-zero angle [23.9°] with the normal to the molecular planes. Projection down the *a* axis reveals the zigzag structure of the chain resulting from the displacement of the Pt atoms by 3.63 Å along *b*. The view perpendicular to the planes of two consecutive molecules in a chain (Fig. 3) emphasizes their relative displacement. Thus, in contrast to the linear-chain structure of the red form of $Pt(bpy)Cl_2$, with nearly equal interplanar [3.40 Å] and Pt···Pt distances [3.45 Å] (Osborn & Rogers, 1974), the Pt···Pt separation [5.291 (1) Å] in $Pt(bpy)I_2$ is considerably longer than the interplanar spacing [3.52 Å]. The C3···C3 [3.445 (17) Å] and Pt···C4 [3.510 (11) Å] distances are the shortest intermolecular contacts. Evidently, significant metal–metal interaction (< 3.5 Å) is precluded by the steric bulk of the I atoms.

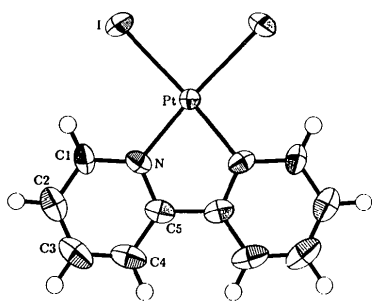


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the molecule with 50% probability ellipsoids showing the atomic numbering system. H atoms are shown as circles of arbitrary size.

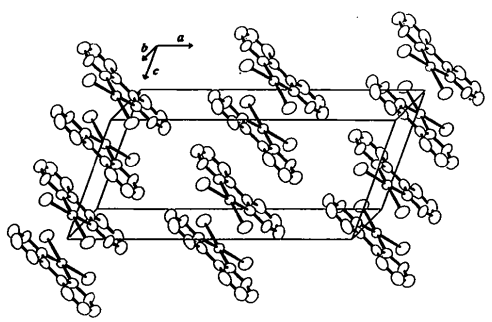


Fig. 2. An *ORTEP*II (Johnson, 1976) drawing of 12 molecules with one unit cell outlined ($Z = 4$). The projection is roughly perpendicular to the *ac* plane, with the *a* axis horizontal; H atoms are not shown.

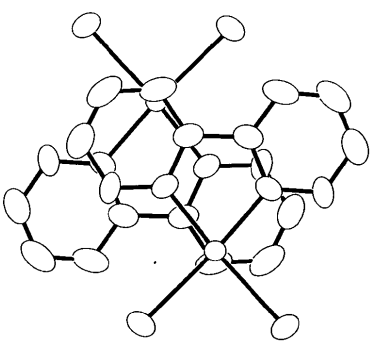


Fig. 3. An *ORTEP*II (Johnson, 1976) drawing of two stacked molecules in the chain. The projection is perpendicualr to the planes of the molecules.

Experimental

The title compound was prepared according to the literature method of Wimmer, Caston, Wimmer & Johnson (1989), and recrystallized from dmf.

Crystal data

$[PtI_2(C_{10}H_8N_2)]$
M_r = 605.08
Monoclinic
$C2/c$
a = 17.400 (4) Å
b = 9.809 (2) Å
c = 7.693 (2) Å
β = 111.97 (2)°
V = 1217.7 (5) Å^3
Z = 4
D_x = 3.30 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 13.5–14.3°
μ = 16.635 mm^{-1}
T = 295 K
Needle
0.350 × 0.099 × 0.092 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
θ–2θ scans
Absorption correction: empirical (ψ scan)
T_{min} = 0.70, T_{max} = 1.31
2332 measured reflections
1070 independent reflections
1070 observed reflections [All reflections]
R_{int} = 0.0176 for 881 duplicate reflections
θ_{max} = 25°
h = −19 → 20
k = −11 → 11
l = −9 → 0
3 standard reflections
frequency: 150 min
intensity variation: within counting statistics

Refinement

Refinement on F^2
$R(F)$ = 0.0316
$wR(F^2)$ = 0.046
S = 2.24
1070 reflections
71 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} < 0.01$
$\Delta\rho_{max}$ = 0.79 e Å^{-3}
$\Delta\rho_{min}$ = −1.23 e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Waber (1974); Cromer (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Pt	0	0.1852 (1)	1/4	0.0320 (1)
I	−0.1015 (1)	0.3755 (1)	0.0689 (1)	0.0603 (2)
N	0.0736 (4)	0.0260 (7)	0.3796 (9)	0.0406 (17)
C1	0.1517 (5)	0.0327 (11)	0.5122 (13)	0.0522 (25)
C2	0.1947 (6)	−0.0830 (14)	0.5917 (16)	0.0660 (29)
C3	0.1616 (7)	−0.2068 (12)	0.5378 (17)	0.0667 (30)
C4	0.0860 (7)	−0.2154 (10)	0.4056 (16)	0.0565 (26)
C5	0.0422 (5)	−0.1013 (9)	0.3249 (12)	0.0417 (19)

Table 2. *Selected geometric parameters* (Å, °)

Pt—I	2.589 (2)	C2—C3	1.341 (17)
Pt—N	2.029 (7)	C3—C4	1.330 (16)
N—C1	1.362 (12)	C4—C5	1.366 (14)
N—C5	1.364 (11)	C5—C5	1.489 (13)
C1—C2	1.370 (15)		
I—Pt—I	87.7 (1)	C3—C2—C1	120.8 (11)
N—Pt—N	79.3 (3)	C4—C3—C2	118.7 (11)
I—Pt—N	175.8 (2)	C5—C4—C3	121.3 (10)
I—Pt—N	96.5 (2)	C4—C5—N	121.2 (8)
C5—N—C1	116.6 (7)	C5—C5—N	113.8 (7)
C2—C1—N	121.3 (9)	C5—C5—C4	125.0 (9)

The Pt atom was located from a Patterson map, while non-H atoms were found by successive structure factor-Fourier calculations. All F_o^2 values were used in the full-matrix least-squares refinement. Coordinates and anisotropic displacement parameters of all non-H atoms and a scale factor were refined. H atoms were placed at calculated positions (C—H = 0.95 Å) with a fixed isotropic displacement parameter and were repositioned several times during the refinement. Weights were taken as $1/\sigma^2(F_o^2)$; variances $[\sigma^2(F_o^2)]$ were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data by propagation of e.s.d. plus another additional term, $(0.014\langle I\rangle)^2$. R = 0.0316 for 1049 reflections with $F_o^2 > 0$ and R = 0.0268 for 956 reflections with $F_o^2 > 3\sigma(F_o^2)$. The final difference map showed the highest peak of 0.79 e Å^{-3} to be within 1.12 Å of the Pt atom and the second highest peak of 0.74 e Å^{-3} to be within 1.72 Å of the I atom. The largest negative peak lies less than 0.69 Å from the I atom. Computer programs used were those of the *CRYM* crystallographic computing system (Duchamp, 1964) and *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71825 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1054]

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